

PATENT SPECIFICATION

(11) 1 466 185

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- (21) Application No. 10074/74 (22) Filed 6 March 1974
 (31) Convention Application No. 339026
 (32) Filed 7 March 1973
 (31) Convention Application No. 442161
 (32) Filed 19 Feb. 1974 in
 (33) United States of America (US)
 (44) Complete Specification published 2 March 1977
 (51) INT CL² C02C 3/00 C05B 11/00 21/00
 (52) Index at acceptance
 C1C 211 215 216 222 223 22X 230 231 233 23X 242 253 306 333
 400 40X 40Y 426
 C1A 13 J210 J241 J244 J270 J271 J285 J320 J340 J342 J3 M12
 N4B T8X6
 C1B 3C3 3CX 3G 4
 C1N 212 213 251 261 269 277 278 328 331 332 335 367 368 377
 389 40Y 742 743 749 757 759 75Y 779 780 78X 78Y
 C3N 25 25K1A 25K1Y



(54) DEWATERING OF SLIMES

(71) We, ANDCO INCORPORATED, a corporation organised and existing under the laws of the State of New York, of 51, Anderson Road, Buffalo, New York 14225, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the dewatering of materials, particularly clayey slimes, such as phosphate rock slimes, which contain high percentages of finely dispersed hydrophilic solid particles in aqueous media, to materials employed for this purpose and to the products so obtained.

The problem of dewatering clayey slimes, slurries and muds containing suspended materials which fail to settle out readily is a very serious one. Especially troublesome is the dewatering of phosphate rock slimes, such as those produced during the mining of phosphate rocks from Florida phosphate deposits. Use of synthetic organic flocculants or coagulants on a dilute slime system to increase rate of settling and eventually consolidate the solid contents up to 5% to 10% has been known and practised widely in water treatments. The most modern polyelectrolyte systems have been designed for such purpose. As the solid content increases beyond 3%, the basic behaviour of slime or sludge changes drastically and the conventional coagulant system can not be effectively used within the allowable economics and it is ineffective. This invention relates to solving this type of problem so that the slime system may be conditioned for fast drainage or instantly changed to

hydrophobic and thus dewatered to high solid content aggregates. In the present mining process of phosphate rock, the matrix, as it is mined, being composed approximately of 1/3 phosphate rock, 1/3 sand or silica tails and 1/3 clayey slimes, on a solid basis, creates a disposal problem.

Because of its hydrophilic nature, the solid content of the clayey slime stored, even after many years, is never above 10% to 15%, and as additional phosphate rock is mined the number of clayey slime ponds increases. These ponds are unattractive and hazardous. They take land out of use, retain water which is often badly needed in the mining areas and require maintenance of the high walls about them to prevent breaks and resultant catastrophic escapes of the slimes. The magnitude of the problem may be better appreciated by noting that in a single year, 1971, in central Florida alone, nine companies produced about 30 million tons of phosphate rock and at the same time, created the problem of disposing of about 30 million tons (solids basis) of slimes. Even at a solids content of as much as 20%, a pond 40 feet deep would have to be of about 5 square miles or 3,000 acres in area to contain this much slime. Of course, the slime entering the pond is at much a lower solids content, usually being at about 3 to 5% solids, and takes about six months to a year to settle to a solids content of as much as 15%. Thus, the slime pond area needed for one year's waste is considerably higher than the five square miles previously mentioned.

In view of the above facts, it is evident that there is a real need for a method which dewateres clayey slimes and converts them to potentially useful industrial products or,

at least, suitable fill. Because of the residual phosphate content of the slimes, if they were in solid form they could be employed as an agricultural material (fertilizer, top dressing, fill) and grass, crops and trees could grow on them. If dewatered, they might also be useful as fillers and aggregates in building materials and other products and as components in cements. In such applications, they are often even more useful when present together with a siliceous material such as sand, e.g., silica tails from phosphate rock mining.

The present invention facilitates the dewatering of phosphate rock slimes or other clayey slimes and suspensions of the kind in which it is difficult to separate the solid particles from the aqueous media. The invention allows the treatment of such materials in an easy, economical manner and results in rapid separation of the solids of the slime from the water thereof, with the ready release from the slime solids of up to as much as 99% or more of the bound water present before treatment. The product obtained is in convenient form and when sand from phosphate rock beneficiation processes is utilized in the treatment of the slime only a single additional treatment material is required, and even this is recoverable to some extent. The product made is useful as an agricultural material or a land fill on which vegetation will grow and has a desired balance of sandy and clayey components.

The history of attempts to solve the phosphate rock slime problem is one of a wide variety of efforts involving expenditures of huge sums of money, millions of dollars, with only failures or half successes resulting. The various methods tried have included chemical flocculation, magnetic flocculation, employment of small high pressure cyclone separators, freezing, electrodecantation, electrophoresis, electrodialysis, sand filtration, mixing of slimes with tailing or overburden, wick stabilization, surcharging, chemical stabilization, shock stabilization (exploding), employment of drying beds, evaporation, use of plant transpiration, and byproduct utilization, as for ground cover, road shoulder and soil conditioning uses. In a report entitled *Electro-Dewatering Tests on Florida Phosphate Rock Slime*, United States Department of the Interior, Bureau of Mines, Report of Investigations 6451 (1964), M. H. Stanczyk and I. L. Feld reported on electro-dewatering experimentation undertaken for the Bureau of Mines, including the use of electro-osmotic vacuum filtration. Their report of the extensive work performed concluded with the statement that they could dewater

the slime only to about 25% solids and the process was slow and power requirements were high; in short, the experiment was unsuccessful.

The interaction of polyelectrolytes and finely divided materials is the subject of much prior art, both in patent specifications or other publications. It is a field given to broad and inconsistent statements at least in part resulting from unwarrantedly broad generalizations based upon fragmentary information in specific fields.

Various other wastes than phosphate slimes also present disposal problems which dewatering can help solve, at least to some extent. As the result of recent water quality laws and regulations and because of water pollution controls, many industries now have to treat their effluents to remove suspended solids and dissolved heavy metals. At present, the metals may be removed by reducing to lower valencies and neutralizing to precipitate them as metal hydroxides. With the precipitated metal hydroxides, dewatering is a serious problem. Even with the most efficient mechanical dewatering devices, such as vacuum filters and centrifuges, only up to 15% solids contents are obtainable. Thus, disposing of such water-containing sludges is a serious (and increasing) problem.

According to the present invention, there is provided a particulate material for dewatering aqueous slimes of dispersed finely divided solid matter, said particulate material comprising solid particles having a size and density such that they are readily separable by gravity from the aqueous medium of the slime, the particles being coated with a polyelectrolyte comprising calcium hydroxide hydrolysed polyacrylamide, as hereinafter defined.

The invention also provides a method of dewatering an aqueous slime of dispersed finely divided solid material, the method comprising intimately contacting the slime with the above particulate material to cause the solid material of the aqueous slime to repel water and adhere to the said particulate material to form a solid phase which is readily separable from the aqueous medium of the slime.

Further in accordance with the invention, there is provided a method of producing aggregate which method comprises contacting a clay with the above particulate material in an aqueous medium whereby to cause the clay to repel water and adhere to the particulate material so as to produce a solid aggregate of clay and particulate material which is readily separable from the aqueous medium.

By utilizing the dewatering procedure of this invention, it has been found that

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sludges can be conditioned to dewater further to obtain higher solids contents and sometimes valuable metal values can thereby be recovered from them.

5 The aggregates of solid material from the slime and particulate material, formed as a result of the process of the invention, and the above clay particulate material aggregates may be used for various applications such as agricultural materials, foundry sands, land fills and in the production of cement and concrete.

10 In the above and following descriptions of the medium being treated and in the claims, for clarity, the single word "slime" is used to describe the medium being treated, which includes difficult to separate finely divided solids in an aqueous medium. It is herein considered as a generic term covering sludges, slurries, suspensions, dispersions, gels, muds and other treated media of thixotropic nature.

15 In preferred embodiments of the invention substantially all the solids of the slime have dimensions less than 100 microns or a composition of an aqueous suspension of ultrafine soil solids associated with the ore, such as, for example, clays, quartz, and minerals which are of sufficiently small particle size so that at least 99% by weight of the solids (dry basis) passes through a 150 mesh screen (United States sieve test).

20 By a polyacrylamide we mean homopolymers of acrylamide and also copolymers of copolymerisable monomeric material of which acrylamide is the predominant component. The polyacrylamide is preferably partially hydrolysed, preferably up to 40% hydrolysed, with calcium hydroxide or hydrated lime to give functional groups containing $-\text{COO}^-\text{Ca}^{++}\text{OOC}-$ and the water solution of polymer has a pH of about 8. The polyacrylamide preferably has a molecular weight of from 100,000 to 15 million, more preferably one million to five million.

25 The particles coated or treated with polyelectrolyte are to be added to the slime system before admixing with particle-slime and are suitably the water insoluble substrates of "tailing sand" which is defined as the solid waste from the flotation step itself in the beneficiation of phosphate rock and is essentially of larger particle size than the slime solids. The particles can also be of plastic material which is ground or chopped in nature. Various cellulose or other filler materials which are homogenous or other mixtures of heterogenous particle substrates can also be used.

30 The polyelectrolyte coagulant preferably forms from 0.0001 to 4%, more preferably from 0.5 to 3% thereof; or about 0.1lb to

3lbs of coagulant per ton of slime on a dry basis.

In one preferred embodiment of the invention, the polyelectrolyte coagulant used as the coating for the particles may also be employed in a primary flocculation step to speed the settling of a less concentrated slime to a higher solids content slime, the latter to be used as the feed in the dewatering process of the invention. Coagulant removed from the aggregates resulting from the dewatering step of the invention may be recycled for use as the coagulant for this pre-treatment step.

35 The slimes to be treated may be those derived from mining, metal finishing, chemical, steel, foundry, paper, textile and other processes and industries. Usually they will include solid components having particle sizes small enough and densities close enough to that of water so that the solids will be difficult to separate from the aqueous media. Normally, it is not feasible to separate such solids from water by filtration because they tend to block filters. In many cases the dispersed solid materials will be clayey and in the usual cases they will be inorganic.

40 Where the slime results from the beneficiation of phosphate rock, the particle sizes or ultimate particle sizes of the clay or other slime component will be that resulting from the normal treatment of phosphate rock matrix to remove slime and tailing sand from it. Usually such particles, which are non-settling, or difficultly settling, are of diameters or have dimensions in the range of about 0.01 to 150 microns. In most cases the maximum dimension will be about 100 microns, with many such products passing entirely through a 200 mesh screen and often through a 325 mesh screen, which particles will be under the 75 and 50 microns, respectively. Of course, the smaller the particle size the more difficult to separate them from aqueous media and so, in many operations it is desired to avoid submicron particles and maintain the lower limit of the slime ultimate particle size at one micron or, if that is not readily possible, at 0.1 micron. The same size ranges apply for slimes other than phosphate rock slimes, too.

45 The concentration of the slimes treated, or the solids contents thereof will usually be from 1 or 2 to 5 or 10%, as received from the plant, with slimes or sludges from primary and secondary treatment sludges, such as industrial wastes, often being at 0.1 to 1% concentration, biological and chemical sludges at about the same concentration and phosphate rock slimes at from 2 to 5% as supplied from the beneficiation plant. By use of coagulants,

- the sludges can be raised to 2 to 6% in the case of industrial sludges and to 2 to 4% for biological and chemical sludges, while phosphate rock slime can be increased to 5 to 15% solids and preferably prior to final dewatering, for the purpose of this invention, will be over 8% in solids when treated to dewater it. However, sludges or slimes as low as 1 to 3% and as high as 25% can be satisfactorily and economically dewatered. In the case of difficult to flocculate minerals of fibrous nature, such as asbestos or attapulgite and bentonite clay, the deatering can be accomplished at low concentrations of 1 to 2% without flocculation to high solids by use of the process of this invention.
- The particulate material utilized to which the polyelectrolyte coating is applied or which is added to the slime before admixing with the polyelectrolyte is of such a size and of a density sufficiently different from that of the aqueous medium of the slimes to be treated so as to be readily gravity-separable therefrom and to be readily separable therefrom when there are adhered to it particles from the slime.
- In some aspects of the invention the particulate material may be of a density lower than that of water, e.g., from 0.2 to 0.9 gram per milliliter, so that with the slime particles adhered thereto, the separated solids will rise through the aqueous medium and be removable at the top, or conversely, the water may be drained from the bottom. However, in most cases it will be preferred to utilize particles of a density greater than that of water or the aqueous medium. Densities in the range of from 1.1 to 3 g./ml. have been found useful and, preferably, the density will be from 1.1 to 2.5 g./ml. For most useful separations the particle sizes will be from about 200 microns to about 4 mm. and preferably will be from 400 microns to 2 mm. in diameter or in minimum dimension.
- Although various materials can be employed as the particulate bases for the coagulant, sand appears to be about the best. It is non-absorbent and so allows the coagulant to have fullest effect on the slime. It can be readily dried and does not form any slimes itself. The sand employed may be from any suitable source and in the case of mining slimes, such as phosphate rock slimes, it is preferred that it be from the original rock matrix. However, sea sand, ore tailings, ground glass and other siliceous materials of equivalent properties are also useful. Among the various other substances which may be employed as the particulate basis for the polyelectrolytes or coagulants are aluminas, activated carbons, graphite, molecular sieves, "urban ore", fly ash, granulated minerals, glass beads, crushed glass, ground slag, titanium dioxide and water insoluble natural and synthetic polymeric materials, e.g., sawdust, ground corn cobs, chopped paper, nylons, polyvinyl chloride, polypropylene, cellulose acetate and polystyrene, either in solid foam forms. The most preferable of these are nonabsorbent and are of spherical, cubical or other substantially regular shape. Continuously moving belt type arrangements can be used to remove "settled" or floated materials and in some cases the belts or portions thereof may be of the described materials treated with polyelectrolyte to continuously remove clay from the aqueous medium. In some cases the coated particles may be continuously carried by the machinery or belts through the medium being treated.
- The coating of the particles with the polyelectrolyte is a simple matter and preferably the coating is effected from an aqueous solution of the polyelectrolyte. Thus, with the concentration usually being from 0.001 to 10% in solvent, more often from 0.1 to 5% in water as the solvent, the particles are coated with the polyelectrolyte by spraying, fogging, dipping, mixing or other suitable procedure, preferably to produce a uniform coating which is from 0.0001 to 1% of the particle weight. Greater quantities of coagulant may be employed, up to 5 or 10%, but normally any excess over 1% is not of sufficient additional activity to warrant the expense. Preferably, the concentration will be from 0.001 to 1% and more preferably, in many cases, it is in the range of 0.05 to 0.5%. It is possible to utilize the coated particles while they are still damp or wet but usually they are dried first, so as to be more free flowing and easier to distribute uniformly throughout a slime. In a continuous system, the nucleic material is mixed with slime solution and simultaneously admixed with polyelectrolyte to dewater and form aggregates.
- The slimes to be treated are any having the characteristic previously described but are preferably those from the mining of phosphate rock and the separation of the phosphate from the matrix thereof. Exemplary materials treatable are the slimes from the rocks described in the Bureau of Mines Report No. 6451, especially at pages 6, 7, and in the Bureau of Mines Report of Investigations No. 6163 (1963) entitled *Chemical and Physical Benefication of Florida Phosphate Slimes*, by James H. Gary, I. L. Feld and E. G. Davis.
- Typically, phosphate rock slimes contain attapulgite, halloysite, kaolinite, apatite, wavellite, bentonite and quartz.
- The mixing of the coated nuclei and the

slime is simply effected and almost any type of mixing equipment will be satisfactory providing that it maintains the slime circulation so that the polyelectrolyte can come into close contact with the finely divided particles of the slime. Right after mixing the polymer treated particles with slime of about 8—10% solid, 60 to 70% of the free water can be decanted off. When the material is press-filtered, then 70 to 80% solid can be obtained instantly.

Treating of the slime may be effected in simple manner. Normally, because of the thickness of the slime, paddle mixers, dough mixers or similar apparatuses having comparatively slow moving mixing parts will be employed, rather than high speed propeller stirrers. The mixing together of the slime and the coated particles may be effected in any order and the main consideration is to obtain good mixing without having the treating materials clump together initially. Although the slime may have a solids content as low as 1% or as high as 25% and providing that it is still fluid, fluidizable or thixotropic, will still be treatable by the present method, it is preferred that the solids content be in the 8 to 15% range. The slime is preferably from the beneficiation plant material, previously settled, but can be from the slime ponds, or materials in the ponds may be treated on site. For example, in large ponds coated sand may be distributed evenly over the slime surface and overnight the surface slime will be dewatered sufficiently for a crust to form, from which water may be removed by pumps, evaporation or other means.

With the slime are mixed the coated particles, with the proportion of coated material to slime treated suitably being from 5:1 to 1:10, preferably 1:1 to 1:5 and most preferably about 1:2 on a solids basis. The temperature of the slime and that of the final mixture may be any suitable temperature, usually being in the range from 10 to 60°C. and most often being in the range from 10 to 40°C. Normally there will be no adjustment of temperature required and the mixing may be effected under ambient conditions or at room temperature. Mixing time may be regulated as desired but normally will be in the range of 30 seconds to eight hours and under the best conditions will be from 30 seconds to five minutes. Settling times thereafter may be the same. After settling is completed, in the case of heavier nuclear particles, the liquid is decanted off, water is expressed from the particles, preferably by means of hydro sieves or screens, and it is found that the solids content, without a drying step, is in the range of 90 to 99%, usually being from 92 to 98% and most often about 95%.

It is not necessary for the particles to be dried for many applications or for disposal but when drying is effected, either by air drying or gravity draining or heating, freely flowing clay coated individual particles are produced. If the product is further heated a rock-like aggregate may be obtained. Also, when the material is compressed and dried, briquettes are obtainable. When individual particles are examined under a microscope, it is seen that the clay has completely covered the surfaces of the nuclei and adheres tightly to them. There is no ready evidence of the presence in the particles of more than a fraction of the coagulant used (usually only 1 to 10% or 2 to 8% is found) and examination of the aqueous phase removed shows that often from 90 to 99% of the coagulant has been released from the nuclei and has dissolved in the aqueous phase, in which form it may be reused, or from which it can be recovered. However, it is within the present invention for the particles to contain larger quantities of the coagulant, too, up to the entire amount charged.

The solid aggregate product resulting is suitable for plant growth immediately, for use in or as cements, fertilizers, sources of P_2O_5 , phosphate charges for electric furnace operations, phosphoric acid sources and derivatives, cinder blocks, and as fillers in various other industrial materials. It may be employed directly as an agricultural product or "soil" on which crops may be grown. In any case, it is easy to dispose of as landfill, for land reclamation. The aqueous phase that separates, containing 90 to 99% of the coagulant, is useful as irrigation water, which has fertilizing properties, may be fed back to the beneficiation or coagulating process, or may have the coagulant removed and reused. In many instances only a portion of the liquid will be returned to the process. It may be returned in a pretreating step in which the slime is coagulated and settled to a higher solids content than normally present, which higher solids content slime is then dewatered. Alternatively, the coagulant-containing liquid may be fed back to an earlier stage in the beneficiation process, such as the water used to help separate the phosphate, siliceous and clayey components of the matrix. Of course, if so desired, none of the liquid is fed back to the process and all is discharged back to the water table, employed for irrigation, or otherwise consumed. When other sludges, such as those containing metal values, usually in the forms of oxides and/or hydroxides, are treated by the described methods recited above, the metal values are recoverable.

The pretreatment step or primary

flocculation previously mentioned is preferably used to increase the solids concentration of phosphate slimes from 1—3% to 5% or more, and preferably to 5 from 8 to 15%, in a short time. Whereas it is known that phosphate slimes will settle after six months to a concentration of about 15% solids, even after years of settling the concentration never passes 25% and often is about 20% or less. Above 35% solids content, the slime takes on the characteristics of a solid. Although the lower solids concentration slimes, e.g., from 1 to 5%, may be treated by the method of this invention without pretreatment, however, in such cases primary flocculation and dewatering of slime step are often combined. Therefore for the clear dewatering of slime, pretreatment is normally desirable and results in a saving in the total amount of polyelectrolyte employed, an increase in treatment process throughput and maximum recovery of usable clear water, and the process can be operated in a continuous manner. Thus, when primary flocculation is carried out in the usual manner, a suitable polyelectrolyte is admixed with a 1 to 3% phosphate slime and the concentration by settling is tripled within from 1 to 20 minutes in laboratory experiments and in actual cases, whereas to attain such concentration by settling alone often takes days. The normal pretreatment settling time of the invention will usually be from two minutes to two hours, preferably from five minutes to one half hour. After treatment to a concentration of 5 to 20%, preferably 8 to 15%, with the slime having a density of about 1.05 to 1.4, it is still thixotropic and may be readily mixed with the treating particles. Instead of utilizing a fresh polyelectrolyte solution for the primary flocculation (such as one of a concentration of from 0.001 to 8%, preferably from 0.01 to 3%) a part of the polyelectrolyte for the primary flocculation may be obtained from recycling the liquid phase recovered from the subsequent dewatering in accordance with the invention.

Although the present process has its most preferable application in the treatment of phosphate rock slimes, the invention is generic to producing clay-sand or clay-particle combinations which may be useful for various functions, including employment as a foundry molding sand. To effect the combination it is only necessary to coat the sand or other particles with the polyelectrolyte and mix the coated particles with clay in an aqueous medium, preferably of about the concentrations previously described. The result is a tightly bonded combination of clay and particles and most of the polyelectrolyte is

redissolved in the medium and may be recycled or removed, or more slime may be continuously added until most of the polymer effectiveness has been utilized.

In comparative experiments, the uses of coagulants, flocculants and polyelectrolytes alone has been tried but often the result was only to thicken the slime even more.

Sand and nuclear materials have been employed but they tend to fall right through the slime and, even when mixed with it by high powered mixers, did not attract slime particles to the sand sufficiently to concentrate the slime to a useful extent, much less to the extent herein described.

The dewatering process of the present invention not only converts the slime to a solid material but causes the instant dewatering of that material. The moisture content of the finished product is exceedingly low, considering its history and the nature of the medium from which it is separated. Separation is easy and although belt types of press filtration may be employed, it is usually not necessary.

One explanation for the exceptional effectiveness of the present invention is that the polyelectrolyte is placed on the surfaces of the particles and thereby attracts the clay or causes it to reject water at a location sufficiently close to the particles so that it can be attracted by them. Then, the polyelectrolyte leaves the surface of the particles to preferentially dissolve in the liquid medium. Alternatively, it may well be that only a minor fraction of the polyelectrolyte employed is needed and remains on the nuclei while the rest of it dissolves. Thus, the product is not loaded with polyelectrolyte.

The following examples illustrate the invention but do not limit it. Unless otherwise stated, all temperatures are in °C. and the units of weight are United States weight units.

EXAMPLE 1

Following a standard procedure for separating the phosphate content of phosphate rock from matrix materials, a central Florida phosphate rock of the type described in Bureau of Mines Report of Investigations No. 6163 is screened to remove oversized particles, after which it is slurried, screened, washed, cyclone separated and floated to produce phosphate as furnace rock, coarse rock, fine rock, and concentrate, plus siliceous tailings, and clayey slime. Various washings and liquid media are recirculated to conserve water. The processes employed are well known in the phosphate rock mining industry and will not be described in detail here especially because the present example relates primarily to dewatering of

only a part of the product. The siliceous tailings and other such materials resulting from the process are dewatered by conventional means, e.g., settling, centrifuging, cyclone separating and sieving, and are then disposed of as landfill or utilized in industrial processes. However, the clayey slime, amounting to about 1/3 of the phosphate rock initially charged, on a solids basis, is difficult to dispose of and previously was sent to large settling ponds, either at the concentration resulting directly from the described process or at a somewhat higher concentration after preliminary settling or solids content increasing operations.

In accordance with the present invention, the resultant slime or dispersion of clayey particles, at a concentration which varies between 1 and 3%, in water, is treated with high molecular weight anionic polyelectrolyte coagulant, in the present case with 0.01 to a 1% aqueous solution, to achieve primary flocculation. This primary flocculation is effected at 30°C., in a conventional settling technique, after which an additional five minutes is allowed for settling. Then, the upper water layer is decanted off and the lower layer is a "concentrated" slime containing 9% to 15% of solids.

To the same mixing vessel containing the thickened slime there is added a calcium hydroxide hydrolyzed polyacrylamide-treated sand, with mixing. The density of the slime is about 1.13 g./ml. and the solids components thereof have dimensions varying over the range of from 0.1 to 50 microns, essentially all of which can pass through a No. 325 mesh screen. The aqueous medium is water with a small percentage of dissolved materials contained. The polyelectrolyte-treated material is of a density of about 1.8 g./ml. and has a nucleus of silica from the phosphate rock silica tailings, the size range of which is from 400 microns to two millimeters. The coating, which is a water-soluble lime or calcium hydroxide hydrolyzed polyacrylamide having a molecular weight 2—5 million, is present on the sand to the extent of about 2.5 g./lb. on a solids basis and the dosage of coagulant is about 1—2 lbs per ton of dry clay. Mixing is continued for about four minutes, after which time the insoluble solids are allowed to separate out for an additional two minutes. Then, the aqueous phase is removed by decantation and the remaining solid product is screened to drain water from it, after which it is air dried. Before air drying a moisture analysis indicates that the moisture content is about 4% and after air drying this is reduced to less than 0.5%.

The friable "clinker" particles produced

are then screened and size reduced to be of the appearance of medium sand, with particles in the 0.5 to 2 millimeter range. As such, it is employed in making concrete (when more finely ground it is used in cements), as a fertilizer material, as a filler in the manufacture of cinder blocks, and sometimes, as the base or nucleus to be coated with polyelectrolyte and used in the treatment of additional slimes. When employed as an agricultural material it is found that within a period of six months the product sustains plant growth and when blended with earth such growth begins immediately and often with vigor.

In a comparative experiment, when the same type of treating materials and thickened slime are used but the sand and polyelectrolyte are applied at the same time but separately to the slime in the mixer no satisfactory separation occurs. In fact, it appears that the slime becomes somewhat thicker. In other comparative experiments, when polyelectrolyte is employed alone a similar unsatisfactory result is obtained and when sand alone is used it falls through the slime to the bottom of the vessel even after mixing, and removes very little of the clayey solids materials from the liquid medium.

Among the polyelectrolytes employed as primary coagulants and/or flocculants which give satisfactory results when used in the manner described in Experiment 1 are: Nalco Nalcolyte 8173, 8174 and 8175; Diamond Shamrock Nopcofloc (Registered Trade Mark) SSC; and Dow Separan (Registered Trade Mark) NP10 and MG200.

EXAMPLE 2

An effluent from a metal finishing process which contains copper, nickel, chromium, zinc and aluminum in low concentrations, e.g., 1 to 10%, as the oxides and hydroxides, is reduced in the usual manner to lower valence compounds. Then the solution is neutralized to a pH of about 8.5, at which all the metal hydroxides are precipitated. To this the coagulant of the previous description and example is added and a sludge of about 3% solid is collected. This sludge behaves much like the phosphate slime described in Example 1.

To this sludge is added polyelectrolyte-coated sand in the ratio of 1:3 sludge: sand, on a solids basis, and mixed with it. The metal hydroxide floc is completely attached to the sand and 80% of the water is collected giving a dewatered sludge. This sludge is dried in air and is mechanically screened to yield the mixed metal hydroxide powders which are subsequently recovered from the sand chemically, by acid

treatment or by other means, to recover the metal values therein.

EXAMPLE 3

The procedures of Examples 1 and 2 are repeated but the polyelectrolyte employed to thicken the dilute slime or sludge is partially obtained from the aqueous medium removed after settling and dewatering of the sand-clay or other aggregate. In another experiment the liquid medium is employed to dissolve additional coating polyelectrolyte for coating of the nuclear particles. In both instances, no difference is discernible between the results obtained with "new" polyelectrolyte and that from the recycled liquid.

EXAMPLE 4

The procedures of Examples 1—3 are repeated, utilizing other calcium hydroxide-hydrolysed polyacrylamide polyelectrolyte, having viscosities in the range of 1,000 to 5,000 centipoises, e.g., those having viscosities of 1,500, 2,500 and 5,000 centipoises, and satisfactory results are obtainable. In further experiments, a polymer of polyacrylamide, maleic anhydride and formaldehyde and also the aluminum complex of such polymer are used. The dewatering operation is satisfactory with such polyelectrolytes, too.

When similar changes are made in the nuclear materials and the sand is replaced with other suitable solids of similar sizes, such as aluminas, activated carbons, graphite, molecular sieves, urban ore (residue clinker from high temperature incineration of municipal refuse), fly ash, granulated minerals, glass beads, crushed glass, ground slag, titanium dioxide, nylon, polyvinyl chloride, polypropylene, cellulose acetate and polystyrene, satisfactory dewatering is effected. This is also the case when foam plastics are utilized which cause the clay-nucleus aggregate to rise through the water and from which the water is drained, rather than decanted. With such materials there may also be used the various other mentioned polyelectrolytes listed earlier in this specification.

EXAMPLE 5

Municipal sludges, metal finishing sludges, foundry waste stream sludges and other chemical and biological sludges, having solids contents in the range of 5 to 15%, are treated according to the method described in Example 2 without pretreatment, and in those cases where lower concentrations of solids are present, such as from 1 to 4%, the pretreatment is utilized. The amounts of polyelectrolyte and coated polyelectrolyte employed are adjusted on a solids content basis. Also,

they are varied over the ranges previously given in the specification and/or with respect to the phosphate rock slime and metal oxide and hydroxide treatment processes. The sludges are satisfactorily dewatered and the solid products obtained are utilized as, for example, fillers and fertilizers, and in some cases, components thereof are chemically recovered for further use in such processes.

EXAMPLE 6

The procedure of Example 1, with respect to the treatment of the thickened slime, is applied to slime in a settling pond, which has a concentration of about 15%. The coated sand is spread evenly over the surface. Surprisingly the coated sand sinks slowly into the surface of the slime and as it sinks it creates clear water channels and the surface of the pond slime becomes coagulated. After overnight standing the pond is completely transformed so as to have a firm surface thereon, with clear water draining off. On top of this, untreated sand and/or soil is/are laid, which is supported by the dewatered material so that the pond is completely reclaimed for agricultural or land development use.

EXAMPLE 7

A foundry sand is made by dewatering a clay-water mix with a polyelectrolyte-covered sand, such as those of the previous examples. The aggregate obtained is employed in the manufacture of molds for casting iron and the molds produced are smoother and result in a smoother casting than ordinary sand, while still being strong enough and resistant enough to heat to be satisfactory replacements for the usual sand of such molds.

EXAMPLE 8

The Large Scale Continuous Dewatering Operation

In accordance with the present invention, the dewatering process follows the following general sequences:

1. Primary Flocculation

A typical discharge usually consists of 1.5 or 3.0% solid. This stream is subjected to primary flocculation by adding 10 to 1000 ppm of high molecular weight anionic polymer and concentrating the solids to 5 or 15% while most of the free water is recovered.

2. Coagulation of High Solid Slimes

The high solid slime resulting from the primary flocculation was subjected to a mixing system by adding $\frac{1}{4}$ to 10 parts of tailing sand to one part of clay and about 1 to 2 pounds of calcium hydrolyzed polymer per ton of dry clay ratio. These three

components are gently mixed until the sand and clay conglomerate and release free water.

In continuous operation, the sand and polymer system were pre-mixed in a continuous moving screen conveyor prior to contact with high solid slimes.

3. Dewatering

The final dewatering of product from step 2 is now discharged into a moving belt filter system which is composed of four separate zones; gravity dewatering of free water zone, draining zone, press zone, and shear zone.

The coagulated sand tailing and phosphate slime dewatered in this manner now consist of 60—80% solid and have good structural strengths.

WHAT WE CLAIM IS:—

1. A particulate material for dewatering aqueous slimes of dispersed finely divided solid matter, said particulate material comprising solid particles having a size and density such that they are readily separable by gravity from the aqueous medium of the slime, the particles being coated with a polyelectrolyte comprising calcium hydroxide hydrolysed polyacrylamide, as hereinbefore defined.

2. A particulate material as claimed in claim 1 in which the particles have a specific gravity of at least 0.1 different from that of water.

3. A particulate material as claimed in claim 2 in which the particles have a density of from 1.1 to 2.5 g./ml.

4. A particulate material as claimed in any one of claims 1 to 3 having minimum particle size in the range 200 microns to 4 mm.

5. A particulate material as claimed in any one of claims 1 to 4 wherein the particles are of sand.

6. A particulate material as claimed in any one of claims 1 to 5 wherein the particles are of a material selected from fly ash, activated carbon, silica, titanium dioxide, alumina, glass, graphite, ground rock, and natural and synthetic polymeric materials which are water insoluble.

7. A particulate material as claimed in any one of claims 1 to 6 wherein the polyacrylamide is up to 40% hydrolysed.

8. A particulate material as claimed in any one of claims 1 to 7 wherein the polyacrylamide has an average molecular weight in the range 100,000 to 15 million.

9. A particulate material as claimed in any one of claims 1 to 8 wherein the polyacrylamide is present in an amount of from 0.0001% to 1% by weight of the particles.

10. A particulate material as claimed in

claim 1, substantially as hereinbefore described and exemplified.

11. A method of dewatering an aqueous slime of dispersed finely divided solid material which comprises intimately contacting the slime with particulate material as claimed in any one of claims 1 to 10 to cause the dispersed solid material of the aqueous slime to repel water and adhere to said particulate material so as to form a solid phase which is readily separable from the aqueous medium of the slime.

12. A method according to claim 11 wherein the solids content of the slime is from 1% to 25%.

13. A method according to claim 11 or claim 12 wherein the solids of the slime have dimensions in the range of 0.01 to 150 microns.

14. A method according to claim 13 wherein substantially all the solids of the slime have dimensions less than 100 microns.

15. A method according to any one of claims 11 to 14 wherein the slime is a clayey slime in water, the particulate material has a specific gravity greater than that of water and the polyelectrolyte is a coagulant for the clayey particles.

16. A method according to any one of claims 11 to 15 wherein the slime is a thixotropic slime from phosphate rock.

17. A method according to claim 16 wherein the phosphate rock slime is phosphate rock slime of typical mineral composition containing attapulgite, halloysite, kaolinite, apatite, wavelite, bentonite and quartz.

18. A method according to claim 16 or claim 17 wherein the particles of the particulate material are of sand from the phosphate rock.

19. A method according to any one of claims 11 to 18 which includes a preliminary step of primary flocculation to concentrate the solids content of the slime.

20. A method according to claim 19 wherein the particulate material and the slime are mixed until the slime solids adhere to the particulate material, the resultant particles are separated from the aqueous phase remaining and are dried, and polyelectrolyte coagulant is released from the particles into the aqueous phase and recycled to the primary flocculation step.

21. A method according to claim 19 or claim 20 wherein in the primary flocculation step the slime at a solids concentration of from 1 to 5% is treated with from 0.0001 to 1%, on a solids basis, of polyelectrolyte to increase the solids content of the slime to a concentration of 8 to 15% and a slime density of 1.05 to 1.4, the

slime of increased solid material content is then mixed with particulate material, and the resultant aggregate is dewatered by gravity and press.

5 22. A method according to any one of claims 11 to 13 wherein the slime is a sludge of metal oxides and hydroxides in water.

23. A method according to claim 22 wherein the metal values of the metal oxides and hydroxides are recovered.

10 24. A method as claimed in claim 11, substantially as hereinbefore described and exemplified.

15 25. A method of producing aggregates of a particulate material and clay which comprises mixing with clay, in aqueous medium, a particulate material as claimed in any one of claims 1 to 10 whereby to cause the clay to repel water and adhere to the particles of the particulate material so as to produce a solid aggregate which is readily separable from the aqueous medium.

20 26. A method according to claim 25 wherein the particulate material is sand, chopped waste plastics or ground corn cobs.

27. A method as claimed in claim 25, substantially as hereinbefore described.

28. A foundry sand comprising the aggregate obtained from the method of claim 26. 30

29. A filler or aggregate for building materials comprising a solid phase obtained by the method of claim 11. 35

30. An agricultural material comprising a solid phase obtained by the method of claim 11 wherein the slime is a phosphate rock slime.

31. A foundry molding sand comprising a solid phase obtained by the method of claim 11 wherein the slime is a clayey slime and the solid particles of the particulate material comprise sand particles. 40

32. A fertilizer including a solid phase obtained by the method of claim 11 wherein the slime is a phosphate rock slime and the solid particles of the particulate material comprise sand particles. 45

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